

The dissolution of the vacancy gas and grain boundary diffusion in crystalline solids

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Abstract

Based on the formula for the number density of vacancies in a solid under the stress or tension, the model of grain boundary diffusion in crystalline solids is developed. We obtain the activation energy of grain boundary diffusion (dependent on the surface tension or the energy of the grain boundary) and also the distributions of vacancies and the diffusing species in the vicinity of the grain boundary.

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Recently, it was shown that sufficiently high pressures as well as mechanical stresses applied to a crystalline solid lead to the decrease in the energy of the vacancy formation and create, therefore, an additional amount of vacancies in the solid [1]. The last effect enhances self-diffusion in the crystal which is normally vacancy-mediated, at least in simple metals. Since large mechanical stresses are normally present in grain boundaries, these new results can elucidate the mechanisms of grain boundary diffusion which have remained so far unclear [2].

According to the thermodynamic equation [3]

$$dE = TdS - pdV, \quad (1)$$

where E is the energy, T is the temperature, S is the entropy, p is the pressure, and V is the volume of a solid, the energy of a solid increases with pressure, so the pressure acts as the energy factor similarly to the temperature. Therefore, the number of vacancies in a solid increases both with temperature and with pressure.

The thermodynamic consideration based on the Clausius- Clapeyron equation gives the number density n of vacancies in a solid in the form [1]

$$n = (P_0/T) \exp(-E_v/T) = (n_0 T_0/T) \exp(-E_v/T), \quad (2)$$

where E_v is the energy of the vacancy formation, $P_0 = n_0 T_0$ is a constant, T_0 can be put equal to the melting temperature of the solid at ambient pressure, and the constant n_0 has an order of magnitude of the number density of atoms in the solid. Here the Boltzmann constant k_B is included in the definition of the temperature T .

The formula (2) describes the thermal expansion of the solid. It should be taken into account that the dissolution of the vacancy gas in a solid causes the deformation of the crystalline lattice and changes the lattice parameters.

The energy of the vacancy formation E_v depends linearly on the pressure P (in the region of high pressures) as given by the formula

$$E_v = E_0 - \alpha P/n_0, \quad (3)$$

where α is a dimensionless constant, $\alpha \approx 18$ for sufficiently high pressures. On the atomic scale, the pressure dependence of the energy of the vacancy formation in the equation (3) is

produced by the strong atomic relaxation in a crystalline solid under high pressure.

With increasing pressure, the number density of vacancies in a solid increases, according to the relation

$$n = (n_0 T_0 / T) \exp(-(E_0 - \alpha P / n_0) / T), \quad (4)$$

and, finally, the vacancies can condense, forming their own sub-lattice. Such is the explanation of the appearance of composite incommensurate structures in metals and some other elemental solids under high pressure [4-7].

Further increase of the number density of vacancies in a solid with increasing pressure leads to the melting of the solid under sufficiently high pressure (and fixed temperature). Such effect has been observed in sodium [6]. In general, such behavior is universal for solids, though the corresponding melting pressure is typically much larger than those for sodium.

We assume that the melting of the crystalline solid occurs when the critical number density n_c of vacancies is achieved. In view of the equation (2), it means that the ratio of the energy of the vacancy formation E_v to the melting temperature T_m of the solid is approximately constant,

$$E_v / T_m \approx \alpha. \quad (5)$$

The value of the constant α in the last relation can be determined from the empirical relation between the activation energy of self diffusion (which is approximately equal to the energy of vacancy formation) and the melting temperature of a solid [8]:

$$E_0 \approx 18T_m, \quad (6)$$

so that $\alpha \approx 18$.

Substituting the expression (3) in the relation (5), we obtain

$$(E_0 - \alpha P / n_0) / T_m \approx \alpha. \quad (7)$$

The last equation gives the melting curve of the crystalline solid in the region of high pressures in the form

$$T + P / n_0 \approx E_0 / \alpha \approx T_0, \quad (8)$$

where T_0 is the melting temperature of the solid at ambient pressure.

The constant n_0 can be determined from the relation between the tensile strength σ_s and the melting temperature T_m of a solid [1]

$$n_0 \cong \sigma_s/T_m. \quad (9)$$

The numerical value of this constant is $n_0 \approx 1.1 \times 10^{22} \text{ cm}^{-3}$ [1].

Replacing in the relation (4) the pressure P by the absolute value of the stress or tension $\sigma = F/S$, applied to a solid, where F is the applied force and S is the cross-section area of the solid in the plane perpendicular to the direction of the applied force, we can estimate the mean number density of vacancies in the solid under the stress or tension:

$$\langle n \rangle \cong (n_0 T_0 / T) \exp(-(E_0 - \alpha \sigma / n_0) / T). \quad (10)$$

The dissolution of the vacancy gas in a solid under the stress or tension is responsible for the low values of the elastic limit and the tensile strength of solids as compared with theoretical estimations not taking into account this process [9].

As indicated above, large mechanical stresses are normally present in grain boundaries. The absolute value σ_b of the mechanical stress in the close vicinity of a grain boundary is given by the formula

$$\sigma_b \cong \gamma_b / r_0, \quad (11)$$

where γ_b is the energy of the grain boundary and r_0 is the radius of the atomic relaxation region (around a vacancy) which will be estimated below.

According to the relation (10), the energy of the vacancy formation in the close vicinity of the grain boundary is given by the formula

$$E_b = E_0 - \alpha \gamma_b / (n_0 r_0). \quad (12)$$

For the small values of misorientation angle $\theta \leq 10 - 15$ degrees, the energy of the dislocation structure contributes to the energy of the grain boundary [10]. However, for larger misorientation angles, the energy of the grain boundary is approximately constant and is determined by the surface tension γ of the solid, $\gamma_b \cong \gamma$.

Due to the Einstein relation between the mobility of an atom, $\mu = v/F$, where v is the velocity of the atom and F is the force acting on the atom, and the diffusion coefficient D [8]:

$$\mu = v/F = D/T, \quad (13)$$

the speed of grain boundary motion v is proportional to the diffusion coefficient D_{\perp} for self-diffusion in the direction perpendicular to the plane of a grain boundary. Therefore, the activation energy E of grain boundary motion is equal to the activation energy E_{\perp} of self-diffusion across the grain boundary. The last activation energy is equal to the activation energy E_b of grain boundary self-diffusion in the case of high-angle grain boundaries, and is approximately equal to the activation energy E_0 of bulk self-diffusion for low-angle grain boundaries. Thus, there is a step of the activation energy for grain boundary motion at some critical value θ_c of the misorientation angle ($\theta_c = 10 - 15^\circ$, as indicated above). Such a step of the activation energy for grain boundary motion has been observed experimentally in high-purity aluminium, the critical value of the misorientation angle being in this case $\theta_c = 13.6^\circ$ [11].

The driving force for grain boundary motion is provided by the distribution of mechanical stresses in a crystalline solid [12].

Assuming that the free surface of a crystalline solid is formed by the plane of vacancies, we can estimate the surface tension of the solid as follows

$$\gamma \cong \beta n_0 E_0 a_0, \quad (14)$$

where $a_0 = n_0^{-1/3} \cong 0.45\text{nm}$ has an order of magnitude of the lattice spacing a , and β is a dimensionless constant which has an order of unity. For hard metals such as Al, Zr, Nb, Fe, Pt, $\beta \cong 0.8$. In the case of mild metals, β is normally smaller, e.g. for Rb and Sr, $\beta \cong 1/4$.

Substituting the estimation (14) for the energy of the grain boundary $\gamma_b \cong \gamma$ in the equation (12), we find

$$E_b \approx E_0 (1 - \beta \alpha a_0 / r_0). \quad (15)$$

Due to the atomic relaxation and thermal motion of atoms, the migration barriers are small [2,13], and the activation energy of self-diffusion is approximately equal to the energy

of the vacancy formation. The analysis of experimental data on the activation energy of grain boundary self-diffusion gives an empirical relation [14]

$$E_b \approx 9T_m \approx E_0/2. \quad (16)$$

From equations (15) and (16), we find the estimation of the radius of the atomic relaxation region,

$$r_0 \approx 2\beta\alpha a_0 \cong \alpha a_0, \quad (17)$$

since β has an order of unity. The radius of the atomic relaxation region has an order of $r_0 \cong 18n_0^{-1/3} \approx 8nm$. This value is comparable with the diameters of tracks produced by high energy ions in metals [15-17]. The grain boundary diffusion width δ [14] is smaller than the radius of the atomic relaxation region due to the non-uniform distribution of vacancies inside the atomic relaxation region in the grain boundary.

If we assume that the mechanical stress σ decreases linearly with the distance x from the plane of the grain boundary,

$$\sigma = \sigma_0 (1 - kx), \quad (18)$$

where σ_0 is the stress at the boundary of the atomic relaxation region with the width r_0 in the grain boundary (this value is smaller than $\sigma_b \cong \gamma/r_0 \cong (1/2)n_0T_m$ and has an order of magnitude $\sigma_0 \cong (1/2)n_0T$), then the equation (10) gives the distribution of vacancies in the vicinity of the grain boundary in the form

$$n \cong (n_0T_0/T) \exp(-(E_0 - \alpha\sigma_0(1 - kx)/n_0)/T) = n_b \exp(-\alpha\sigma_0 kx/(n_0T)), \quad (19)$$

where n_b is the number density of vacancies at the boundary of the atomic relaxation region.

Due to the trapping by vacancies [18], the distribution of the concentration c of the diffusing species in the vicinity of the grain boundary follows the same law:

$$c \cong c_b \exp(-x/l), \quad (20)$$

where c_b is the concentration of the diffusing species at the boundary of the relaxation region, and the scale l is given by the formula

$$l = n_0 T / (\alpha \sigma_0 k) . \quad (21)$$

Here k has an order of magnitude of $1/d$, d being the size of the grain, so that $l \cong d/\alpha$. The penetration profiles described by the equation (20) have been indeed observed experimentally in the case of grain boundary diffusion in metals [8, 18], the measured penetration depth l having an order of a few micrometers [8].

To summarize, we obtained the dependence of the activation energy of grain boundary self-diffusion on the energy of the grain boundary, the estimation of the surface tension of a solid and of the energy of the grain boundary, and the width of the atomic relaxation region in the grain boundary (or the radius of the atomic relaxation region around a vacancy). We obtained further the distributions of vacancies and the diffusing species in the vicinity of the grain boundary. The obtained radius of the atomic relaxation region is consistent with the diameters of tracks produced by high energy ions in metals.

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